EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Understanding sulphur dissolution and re-deposition and microstructural evolution in lithium sulphur batteries by in operando X-ray diffraction computed tomography	**Experiment number**: MA3400
Beamline: ID15	**Date of experiment**: from: 15 Nov 17 to: 19 Nov 17	**Date of report**: 19 Mar 18
Shifts: 12	**Local contact(s)**: Marco Di Michiel	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

***Chun Tan (University College London)

Paul Shearing (PI) (University College London)

Report:

Lithium sulphur (Li-S) batteries offer superior theoretical specific capacity, lower cost and enhanced safety compared to incumbent Li-ion battery technology. However, the multiple reaction stages and phase changes result in a multitude of challenges including active material loss that significantly impact cycling life. Through the 3D visualization of the sulphur cathode, a wealth of information such as microstructural evolution of the different phases at various states of charge (SoC) with cycling can be obtained. In operando techniques, only achievable at synchrotron sources, allow sufficiently high temporal resolution to enable visualization at different SoC by negating self-discharge issues significant in Li-S cells. In this experiment, we have used high temporal resolution synchrotron XRD-CT to capture the microstructural evolution of sulphur particles and carbon host and chemical transition of elemental sulphur (S) to lithium sulfide (Li_2S) as a function of state of charge.

At ID15 we achieved a better than 1 µm x 1 µm monochromatic beam at 50 keV, and an acquisition rate of up to 100 Hz using the detector with the set-up shown in Figure 1(a). The high speed photon counting Pilatus Dectris CdTe 2M detector available at the ESRF, in combination with our bespoke XRD-CT cell fabricated in PEEK as shown in **Figure 1(b) and (c)**, enabled us to reach an acquisition rate of up to 100 Hz per raster point. As illustrated in Figure 1(b), the PEEK cell body was narrowed down to 2.5 mm outer diameter, containing an elemental sulfur cathode and lithium metal anode of ca. 1.5 mm diameter to maximize the signal to noise ratio of the resulting diffraction patterns. In one experiemental configuration, XRD-CT slices of the sulfur electrode were acquired *in-situ* at regular intervals of SoC, along with complementary absorption CT tomograms at 100% and 0% SoC. In another experimental configuration, XRD-CT volumes were throughout the depth of the electrode as a function of SoC to study depth related microstructural evolution. For both configurations, coarse scans of the whole cell with 20 µm step size were acquired alongside smaller regions of interest with 1 µm step size. However, we were unable to complete the full set of experiments planned for this beamtime despite the best efforts of the beamline staff (who went out of their way to resolve this issue, even at odd hours) due to severe networking issues with the ESRF cluster that was beyond their control. This resulted in the frequent occurrence of missed frames during acquisitions that required repeat measurements.

Preliminary reconstructions of the coarse whole cell scans are shown in Figure 2 and are indicative of the success of this experiment, showing large agglomerates of the crystalline S_8 phase in the fully charged cell in Figure 2(a), and what we believe to be crystalline Li_2S in the fully discharged cell in Figure 2(b). Whilst the nano-sized Li_2S crystals formed during discharge are below the spatial resolution of this technique, we expect to be able to observe volume averaged diffraction patterns characteristic of Li_2S within each voxel.

The high flux and high energy capabilities of ID15, and the expertise and deep involvement of the ID15A beamline staff, especially Marco Di Michiel and Antony Vamvakeros, contributed significantly to make this novel experiment possible.

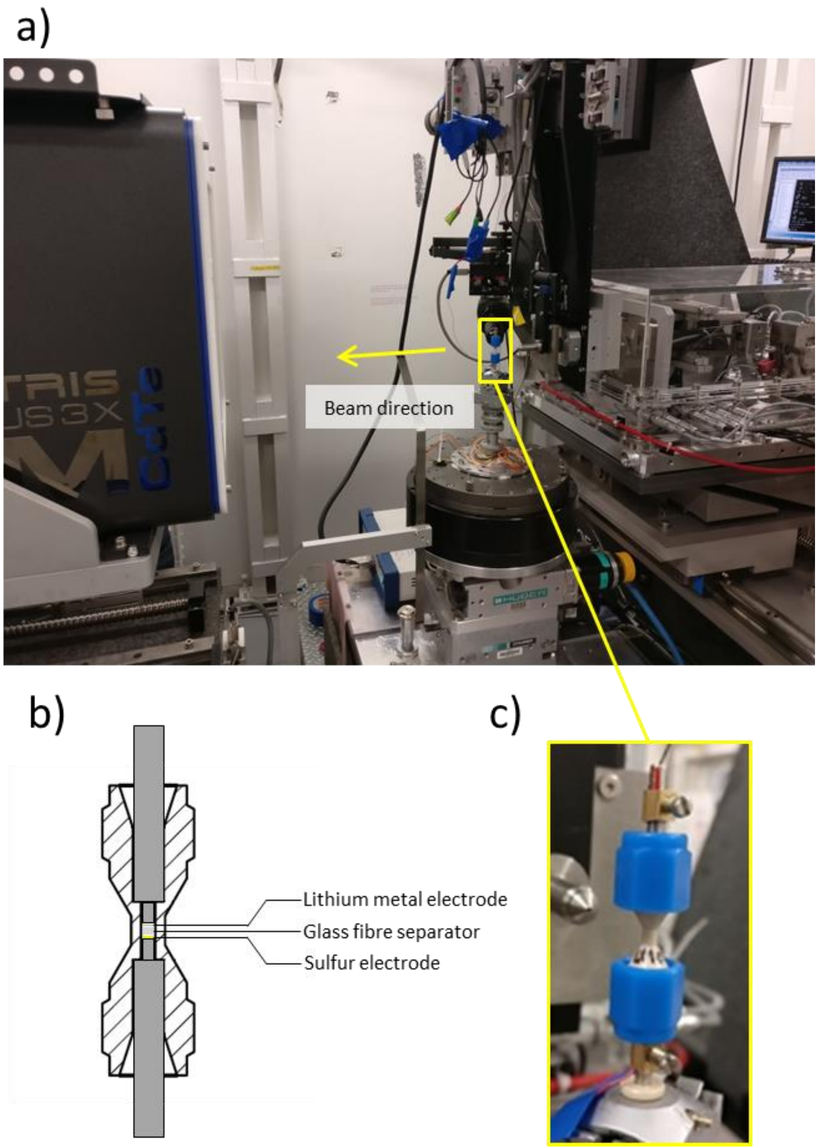

Figure 1: (a) Experimental set-up in the ID15A hutch showing the Pilatus Dectris 3X CdTe 2M detector. (b) Cross-section of PEEK XRD-CT cell showing the electrodes and current collector pins. (c) PEEK XRD-CT cell with electrical connections attached.

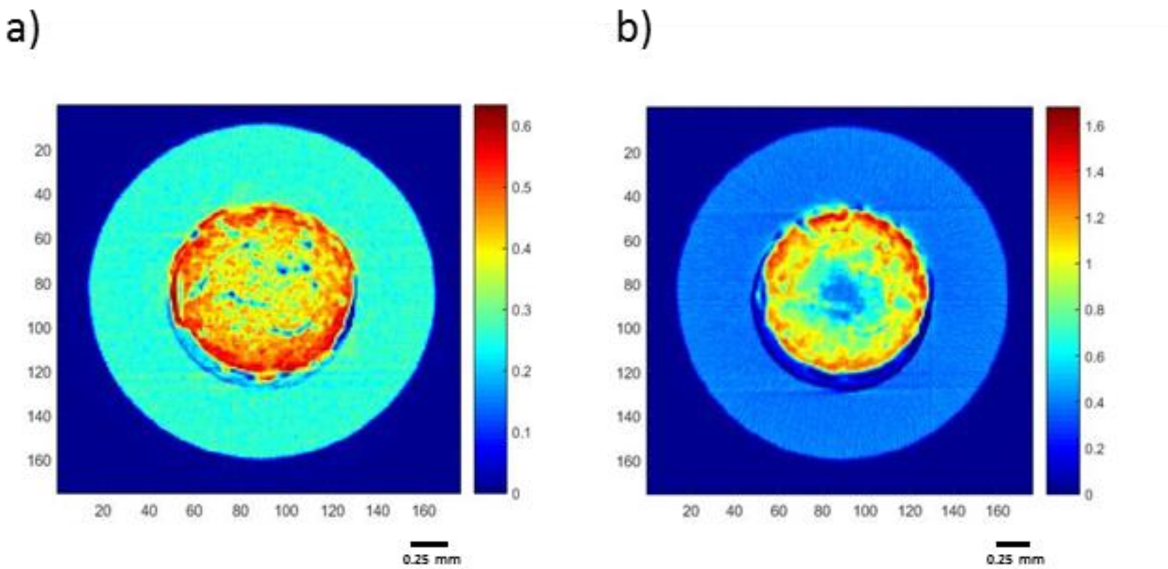

Figure 2: Coarse reconstructions of a single slice in an XRD-CT scan showing (a) the fully charged cell at ca. q =0.82 A^{-1} corresponding to the (1 1 1) reflection of orthorhombic S_8, and (b) the fully discharged cell at ca. q=1.89A^{-1}, corresponding to the (1 1 1) reflection of Li_2S.